

Docket  
Q198-US1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

WEST, Robert C. et al.

Serial No.: 10/810,019

Filed: March 25, 2004

For: POLYSILOXANE FOR USE IN  
ELECTROCHEMICAL CELLS



Group No.: 1745

Examiner: CREPEAU, Jonathan

Docket No.: Q198-US1

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

DECLARATION BY ROBERT C. WEST, ZHENGCHENG ZHANG, AND KHALIL  
AMINE UNDER 37 CFR 1.131

Sir:

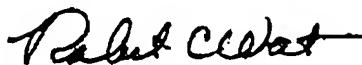
I, Robert C. West, Zhengcheng Zhang, or Khalil Amine, hereby declare and state as follows:

1. I am an inventor of patent application serial number 10/810,019.
2. I am either the "Dr. West," "Dr. Amine," or Dr. Zhang mentioned in the e-mail attached as exhibit A (the e-mail).
3. The e-mail includes an attachment (the attachment).
4. The redacted document attached as exhibit B is an accurate reproduction of the attachment.
5. I hereby declare that all statements made herein of my own knowledge are true, and the statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Docket  
Q198-US1

Date: *October 3 2007*

Respectfully submitted:



Robert C. West

Date:

Zhengcheng Zhang

Date:

Khalil Amine

EXHIBIT A

**Lisa Robbins**

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**From:** Wang, Qingzheng [wangq@cmt.anl.gov]  
**Sent:** Tuesday, February 03, 2004 11:17 AM  
**To:** Liz Bush  
**Cc:** lisdodd@aol.com; Amine, Khalil  
**Subject:** Q203\_Draft  
**Attachments:** Q203-XX1Draft02-02-04\_revised\_ANL.doc

Hello, Liz and Travis:

I have incorporated comments from Dr. West, Dr. Amine, Dr. Zhang, and myself into the attached revised version (changes made in blue). Please note I also made changes to some graphs so that they are related to what is described in the text. Please let me know if you have any questions.

Have a nice Day!

Best Wishes.

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**EXHIBIT B**

## SILOXANE BASED ELECTROLYTES FOR USE IN ELECTROCHEMICAL DEVICES

### REFERENCE TO RELATED APPLICATIONS

- [0001] This application is a continuation-in-part of U.S. Patent Application serial number XXX.
- [0002] This application is related to XXX.

### STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0003] This invention was made with United States Government support under NIST ATP Award No. 70NANB043022 awarded by the National Institute of Standards and Technology (NIST). The United States Government has certain rights in this invention pursuant to NIST ATP Award No. 70NANB043022 and pursuant to Contract No. W-31-109-ENG-38 between the United States Government and the University of Chicago representing Argonne National Laboratory, and NIST 144 LM01, Subcontract No. AGT DTD 09/09/02.

### FIELD

[0004] The present invention relates to electrolytes for electrochemical devices, and more particularly to siloxane based electrolytes.

### BACKGROUND

[0005] The increased demand for lithium batteries has resulted in research and development to improve the safety and performance of these batteries. Many batteries employ organic carbonate electrolytes associated with high degrees of volatility, flammability, and chemical reactivity. A variety of polysiloxane based electrolytes have been developed to address these issues. However, polysiloxane based electrolytes typically have a low ionic conductivity that limits their use to applications that do not require high rate performance.

### SUMMARY

[0006] An electrochemical device is disclosed. The device has an electrolyte that includes a siloxane activating an anode and a cathode. The one or more siloxanes have two or three silicons.

At least one of the silicons is linked to one or more side chains that include a poly(alkylene oxide) moiety. The electrolyte can be a solid or a liquid. In some instances, the device is a secondary battery.

[0007] A method of forming an electrochemical device is also disclosed. The method includes generating an electrolyte that includes a siloxane having two or three silicons. At least one of the silicons is linked to one or more side chains that include a poly(alkylene oxide) moiety. The method also includes activating at least one anode and at least one cathode with the electrolyte.

[0008] The electrolyte can optionally include one or more components in addition to the siloxane. In one example, the electrolyte includes at least one additive selected from the group consisting of: vinyl carbonate, vinyl ethylene carbonate, ethylene sulfite, 2,3-dimethyl-1,3-butadiene, styrene carbonate, aromatic carbonates, vinyl pyrrole, vinyl piperazine, vinyl piperidine, vinyl pyridine, and mixtures thereof. In one example, the electrolyte includes vinyl ethylene carbonate as an additive.

[0009] The electrolyte can include a cross linked network polymer that forms an interpenetrating network with the siloxane. The network polymer can include a cross-linked polyacrylate or a cross-linked polymethacrylate.

[0010] In some instances, the electrolyte includes one or more solid polymers that are solids at room temperature. The one or more solid polymers can include at least one component selected from the group consisting of: polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene), polystyrene, polyvinyl chloride, poly(alkyl methacrylate), poly(alkyl acrylate), styrene butadiene rubber (SBR), poly(vinyl acetate), poly(ethylene oxide) (PEO) and mixtures thereof.

## BRIEF DESCRIPTION OF THE FIGURES

[0011] Figure 1 illustrates a method of forming a siloxane having two silicons and two side chains that each include a polyethylene oxide moiety.

[0012] Figure 2A is a  $^{29}\text{Si}$  NMR spectrum for a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety.

[0013] Figure 2B is  $^1\text{H}$  NMR for a plurality of siloxanes that each have two silicons and side chains that include a poly(ethylene oxide) moiety.

[0014] Figure 3A illustrates ionic conductivity versus temperature for a plurality of different electrolytes. Each electrolyte includes  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI) dissolved in a siloxane having two silicons and side chains that includes a poly(ethylene oxide) moiety.

[0015] Figure 3B illustrates ionic conductivity versus temperature for an electrolyte that includes LiTFSi dissolved in a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety.

[0016] Figure 3C illustrates ionic conductivity versus temperature for an electrolyte that includes lithium bis(oxalato)borate (LiBOB) dissolved in a siloxane having two silicons and a side chain that includes a poly(ethylene oxide) moiety.

[0017] Figure 4 illustrates results of cyclic voltammetry performed on an electrolyte having LiTFSi dissolved in a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety. The electrolyte was stable up to 4.5 V without significant decomposition.

[0018] Figure 5 illustrates a charge/discharge profile for a lithium secondary cell having a Li metal anode and a cathode activated by an electrolyte that includes lithium bis(oxalato)borate (LiBOB) dissolved in a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety. The composition of the cathode was 84wt%  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black.

[0019] Figure 6 illustrates an initial charge/discharge profile for a lithium secondary cell having an anode and a cathode activated by an electrolyte having LiBOB dissolved in a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety. The composition of the cathode was 84wt%  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black. The composition of the anode was 92wt% meso carbon micro beads (MCMB) and 8wt% PVDF binder.

[0020] Figure 7 illustrates the cycling performance of a lithium secondary cell having a Li metal anode and a cathode activated by an electrolyte having LiBOB dissolved in a siloxane having three silicons and a side chain that includes a poly(ethylene oxide) moiety. The composition of the cathode was 84wt%  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black.



## DESCRIPTION

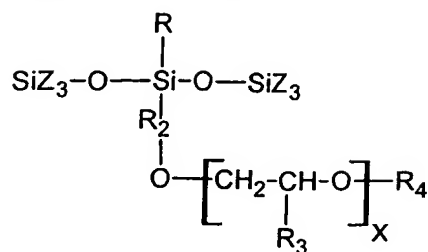
[0021] An electrolyte suitable for use in electrochemical devices is disclosed. The electrolyte includes a siloxane having two or three silicons. The siloxane includes one or more side chains that each include a poly(alkylene) oxide moiety. These siloxanes can be less volatile, flammable and chemically reactive than the organic carbonate electrolytes that are often employed in batteries. Accordingly, electrolytes that include these siloxanes are better suited for use as a battery electrolyte than organic carbonates.

[0022] The one or more poly(alkylene oxide) moieties can help dissolve lithium salts that are employed in batteries. Accordingly, these siloxanes can provide an electrolyte with a concentration of free ions suitable for use in batteries. Additionally, the one or more poly(alkylene oxide) moieties can enhance the ionic conductivity of the electrolyte at room temperatures. For instance, the electrolyte can provide an ionic conductivity higher than  $2.0 \times 10^{-4}$  S/cm at 24 °C.

[0023] The electrolyte can be a liquid, a solid or a gel. The siloxanes are generally liquids at room temperature. As a result, the electrolyte can be a liquid. Further, the electrolyte can include a cross-linked network polymer that forms an interpenetrating network with the siloxane. An electrolyte that includes an interpenetrating network can be a solid or a gel. Accordingly, the cross-linked network polymer can serve as a mechanism for providing a solid electrolyte or a gel electrolyte. Alternately, the electrolyte can include one or more solid polymers in addition to the siloxane. The one or more solid polymers are a solid when standing alone at room temperature. The solid polymer can be employed to generate a gel electrolyte or a solid electrolyte such as a plasticized electrolyte.

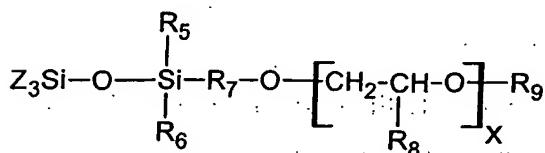
[0024] When the electrolyte is a liquid, the siloxane can provide the electrolyte with a viscosity that is reduced relative to polysiloxane based electrolytes. The reduce viscosity can improve wetting of electrodes in an electrochemical device and can enhance the homogeneity of the electrolyte distribution in the cell. These electrolyte features can lead to increased capacity and enhanced cycling properties in batteries. As a result, the electrolytes can be suitable for use in batteries such as high-energy and long cycle life lithium secondary batteries, such as biomedical devices, electrical vehicles and satellite applications.

[0025] Formula I illustrates a suitable siloxane having three silicons. Formula I:



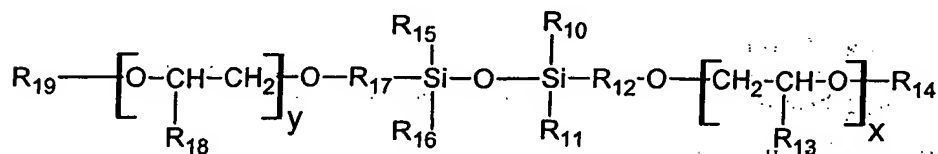
where R is an alkyl group; R<sub>2</sub> is a spacer; R<sub>3</sub> is a hydrogen atom or an alkyl group; R<sub>4</sub> is an alkyl group; Z is an alkyl or an aryl group and the Zs can be the same or different and x is from 1 to 30. The spacer can be an organic spacer and can include one or more -CH<sub>2</sub>- groups. Other suitable spacers can include an alkylene, alkylene oxide or a bivalent ether group. These spacers can be substituted or unsubstituted. In one example, R<sub>2</sub> has a structure according to: -(CH<sub>2</sub>)<sub>3</sub>-. In another example, Z, R and R<sub>4</sub> are each a methyl group. In a preferred example: Z, R and R<sub>4</sub> are each a methyl group; R<sub>2</sub> has a structure according to: -(CH<sub>2</sub>)<sub>3</sub>-; R<sub>3</sub> is a hydrogen; and x is 7.

[0026] Formula II illustrates a suitable siloxane having two silicons. Formula II:



where R<sub>5</sub> is an alkyl group; R<sub>6</sub> is an alkyl group; R<sub>7</sub> is a spacer; R<sub>8</sub> is a hydrogen atom or an alkyl group; R<sub>9</sub> is an alkyl group; Z is an alkyl or an aryl group and the Zs can be the same or different and x is from 1 to 30. The spacer can be an organic spacer and can include one or more -CH<sub>2</sub>- groups. Other suitable spacers can include an alkylene, alkylene oxide or a bivalent ether group. These spacers can be substituted or unsubstituted. In one example, R<sub>7</sub> has a structure according to: -(CH<sub>2</sub>)<sub>3</sub>-. In another example, Z, R<sub>5</sub>, R<sub>6</sub> and R<sub>9</sub> are each a methyl group.

[0027] Formula III illustrates a suitable siloxane having two silicons. Formula III:



where R<sub>10</sub> is an alkyl group; R<sub>11</sub> is an alkyl group; R<sub>12</sub> is a spacer; R<sub>13</sub> is a hydrogen atom or an alkyl group; R<sub>14</sub> is an alkyl group; R<sub>15</sub> is an alkyl group; R<sub>16</sub> is an alkyl group; R<sub>17</sub> is a spacer; R<sub>18</sub> is a hydrogen atom

or an alkyl group;  $R_{19}$  is an alkyl group;  $x$  is from 1 to 30 and  $y$  is from 1 to 30. The spacers can be the same or different. Each spacer can be an organic spacers and can include one or more  $-CH_2-$  groups. Other suitable spacers can include an alkylene, alkylene oxide or bivalent ether. These spacers can be substituted or unsubstituted. In one example,  $R_{12}$  and  $R_{17}$  each has a structure according to:  $-(CH_2)_3-$ . In another example,  $R_{10}$ ,  $R_{11}$ ,  $R_{14}$ ,  $R_{15}$ ,  $R_{16}$ , and  $R_{19}$ , are each a methyl group. In another example,  $R_{19}$  and  $R_{14}$  have the same structure,  $R_{18}$  and  $R_{13}$  have the same structure,  $R_{17}$  and  $R_{12}$  have the same structure and  $R_{10}$ ,  $R_{11}$ ,  $R_{15}$  and  $R_{16}$  have the same structure.

[0028] The siloxanes can be generated by employing a hydrosilylation between a siloxane precursor having silicons bonded to one or more hydrogens and an allyl terminated side chain precursor that includes a poly(alkylene oxide) moiety. For the purposes of illustration, Figure 1 illustrates a method of employing hydrosilylation to generate siloxanes according to Formula III. A precursor siloxane labeled A and a side-chain precursor labeled B are mixed to form a precursor solution. The precursor siloxane includes two silicons. Each of the silicons are linked to a hydrogen. The side-chain precursor includes an allyl-terminated spacer precursor represented by  $-R_{20}-CH=CH_2$  where  $R_{20}$  can be nil or organic. For instance,  $R_{20}$  can include one or more  $CH_2$  groups. Further,  $R_{20}$  can include an alkylene, alkylene oxide or a bivalent ether moiety and can be substituted or unsubstituted. In one example,  $R_{20}$  represents  $-CH_2-$ . The remaining variables shown in Figure 1 are defined with respect to Formula III.

[0029] In some instances, a reaction solvent is added to the precursor solution of Figure 1. A suitable solvent includes, but is not limited to, toluene, THF, and benzene. A catalyst can be added to the precursor solution to catalyze the hydrosilylation reaction. Suitable catalysts for use in the precursor solution include, but are not limited to, platinum catalysts such as Karstedt's catalyst (divinyltetramethyldisiloxane (Pt(dvs))), dicyclopentadiene platinum(II) dichloride,  $H_2PtCl_6$ . In some instances, heat is applied to the precursor solution to react the components of the precursor solution. The reaction can be continued until the Si-H groups are no longer evident on an FTIR spectrum. The product solution can be distilled to remove any unreacted side-chain precursors and/or reaction solvent.

[0030] The method of Figure 1 can be adapted to provide a siloxane having side chains with different structures. For instance, the precursor solution can be prepared so as to include side chain precursors having different structures. At least a portion of the product siloxanes will

include side chains having different structures. The method of Figure 1 can also be adapted to generate a siloxane having a silicon linked to more than one side chain. For instance, a siloxane precursor including one or more silicons linked to more than one hydrogen can yield a siloxane having one or more silicons linked to more than one side chain.

[0031] The electrolytes can include a single siloxane. Alternately, the electrolyte can include two or more siloxanes. In some instances, at least one of the two or more siloxanes is chosen from those represented by Formulas I through Formulas III. Alternately, each of the siloxanes can be chosen from those represented by Formulas I through Formulas III. In one example, a first siloxane is selected to keep the viscosity low and a second siloxane is selected to enhance voltage stability. As another example, a highly conductive siloxane may be combined with a low viscosity siloxane to improve wetting of electrodes, leading to increased capacity and enhanced cycling properties.

[0032] The electrolyte can be prepared by dissolving one or more salts in one or more siloxanes. The electrolyte can be prepared such that the concentration of the salt in the electrolytes is about 0.3 to 2.0 M, about 0.5 to 1.5 M, or about 0.7 to 1.2 M. Suitable salts for use with the electrolyte include, but are not limited to, alkali metal salts including lithium salts. Examples of specific lithium salts include  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ , lithium alkyl fluorophosphates, lithium bis(chelato)borates including lithium bis(oxalato)borate ( $\text{LiBOB}$ ) and mixtures thereof.

[0033] When a lithium salt is used with the electrolyte, an  $[\text{EO}]/[\text{Li}]$  ratio can be used to characterize the salt in the electrolyte.  $[\text{EO}]$  is the molar concentration in the electrolyte of the ethylene oxides in the one or more siloxanes. Because  $[\text{EO}]$  is directed to ethylene oxides, there are at least  $x$  ethylene oxides in the siloxanes according to Formulas I and Formulas II while there are at least  $x + y$  ethylene oxides in the siloxanes according to Formulas III. In some instances, the spacers will also include ethylene oxides. For instance, a side chain according to Formula I has  $x+1$  ethylene oxides when  $\text{R}_2$  is  $-(\text{CH}_2)_3-$ . The electrolyte is preferably prepared so as to have a  $[\text{EO}]/[\text{Li}]$  ratio of 5 to 50. When the  $[\text{EO}]/[\text{Li}]$  ratio is larger than 50, the ionic conductivity of the resulting electrolyte can become undesirably low because few carrier ions are in the electrolyte. When the  $[\text{EO}]/[\text{Li}]$  ratio is smaller than 5, the lithium salt may not sufficiently dissociate in the resulting electrolyte and the aggregation of lithium ions can confine the ionic conductivity.

[0034] In some instances, one or more additives are added to the one or more siloxanes. Additives can serve a variety of different functions. For instance, additives can enhance the ionic conductivity and/or enhance the voltage stability of the electrolyte. A preferable additive forms a passivation layer on one or more electrodes in an electrochemical device. The passivation layer can enhance the cycling capabilities of the electrochemical device. In one example, the passivation layer is formed by reduction of the additive at the surface of an electrode that includes carbon. In another example, the additive forms a polymer on the surface of an electrode that includes carbon. The polymer layer can serve as the passivation layer.

[0035] Suitable additives include, but are not limited to, carbonates, sulfur compounds, unsaturated hydrocarbons and nitrogen compounds. In some instances, the electrolyte includes at least one additive selected from the group consisting of: vinyl carbonate (VC), vinyl ethylene carbonate (VEC), ethylene sulfite, 2,3-dimethyl-1,3-butadiene, styrene carbonate, aromatic carbonates, vinyl pyrrole, vinyl piperazine, vinyl piperidine, vinyl pyridine, and mixtures thereof. In one example, the electrolyte includes vinyl ethylene carbonate as an additive. VC is an example of an additive that can be reduced at the surface of an electrode that includes carbon to form a passivation layer that includes a carbonate. Pyridine is an example of an additive that can form a polymeric passivation layer at the surface of an electrode that includes carbon. VEC is an example of an additive that can form a passivation layer by both being reduced and forming a polymer at the surface of an electrode that includes carbon. [REDACTED]

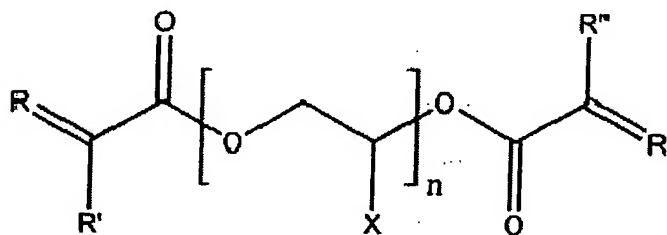
[REDACTED] A suitable concentration for an additive in the electrolyte includes, but is not limited to, concentrations greater than 0.1 wt%, greater than 0.5 wt% and/or less than 5 wt% or less than 20 wt%.

[0036] A preferred embodiment of the electrolyte includes one or more of the siloxanes, a lithium(oxalato)borate (LiBOB) salt and one or more additives selected from a group consisting of VC and VEC.

[0037] The electrolyte can include a network polymer that forms an interpenetrating network with the siloxane. An electrolyte having an interpenetrating network can be generated by polymerizing and/or cross-linking one or more network polymers in the presence of the siloxane. Alternately, an electrolyte having an interpenetrating network can be generated by polymerizing and/or cross-linking one or more network polymers and the siloxane in the presence of one another.

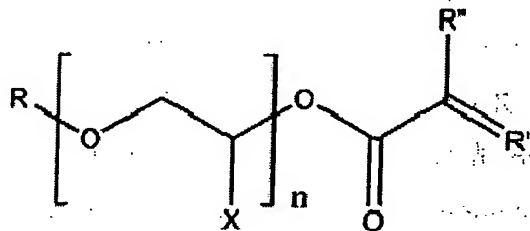
[0038] Suitable network monomers from which the network polymer can be formed include, but are not limited to, acrylates and methacrylates. Acrylates and/or methacrylates having one or more functionalities can homopolymerize to form a polyacrylate and/or a polymethacrylate network polymer. Acrylates and/or methacrylates having two or more functionalities can both polymerize and cross-link to form a cross-linked polyacrylate network polymer and/or to form a cross-linked polymethacrylate network polymer. In some instances, acrylates and/or methacrylates having four or more functionalities are a preferred network monomer. Suitable acrylates include, but are not limited to, poly(alkylene glycol) dialkyl acrylate. Suitable methacrylates include, but are not limited to, poly(alkylene glycol) dialkyl methacrylate.

██████████ A suitable network monomer is represented by the following Formula IV:



wherein R is an alkyl group having 1 to 10 carbon atoms; R' represents hydrogen or a group selected from an alkyl group having 1 to 10 carbon atoms and/or an alkenyl group having 2 to 12 carbon atoms; R'' represents hydrogen or a group selected from an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; X is hydrogen or a methyl group; and n represents a numeral of 1 to 15. ██████████

[0040] When a monomer that cross-links is employed to form a cross-linked network polymer, a control monomer can be employed to control cross-linking density. A suitable control monomer for use with a network monomer according to Formula IV is represented by the



following Formula V:

where R is an alkyl group having 1 to 10 carbon atoms, R' is an alkyl group having 1 to 10 carbon atoms; R'' is hydrogen or a group selected from an alkyl group having 1 to 10 carbon atoms or an alkenyl group having 2 to 12 carbon atoms; X is hydrogen or a methyl group; and n represents a whole number from 1 to

20. ██████████ During formation of the network polymer,

the illustrated control monomer serves as a 'co-monomer' with the network monomers according to Formula IV. Because the control monomer does not cross link, increasing the amount of control monomer present during formation of the network polymer can reduce the density of cross linking. [REDACTED]

[0041] Diallyl terminated compounds can also be employed as a network monomer. Diallyl terminated compounds having four or more functionality can polymerize and cross-link. As an example, the carbonyl groups shown in Formula IV can be replaced with  $\text{CH}_2$  groups to provide a diallyl terminated compound having four functionalities that allow the compound to polymerize and cross link. The carbonyl groups shown in Formula V can be replaced with  $\text{CH}_2$  groups to provide an example of a control monomer for controlling the cross linking density of the diallyl terminated compound. [REDACTED]  
[REDACTED]  
[REDACTED]  
[REDACTED]  
[REDACTED]

[0042] An electrolyte that includes an interpenetrating network can be formed by generating a precursor solution that includes the siloxane, the monomers for forming the cross-linked network polymer and one or more salts. Suitable salts include, but are not limited to,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ,  $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$ ,  $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ , lithium bis(chelato)borate including lithium(oxalato)borate ( $\text{LiBOB}$ ), and lithium alkyl fluorophosphates. The precursor solution can also optionally be generated so as to include one or more radical initiators and/or one or more additives. Suitable radical initiators include, but are not limited to, thermal initiators including azo compounds such as azoisobutyronitrile, peroxide compounds such as benzoylperoxide, and bismaleimide. A control monomer can also optionally be added to the precursor solution to control the cross-linking density of the network monomer. In some instance, the temperature of the precursor solution is elevated and/or the precursor solution is exposed to UV to form the electrolyte. The resulting electrolyte can be a liquid, solid or gel. The physical state of the electrolyte can depend on the ratio of the components in the precursor solution.

[0043] In an electrolyte formed using the monomers represented by Formula IV, the network polymer is formed from a monomer that homopolymerizes and cross-links. Alternately, an

electrolyte having an interpenetrating network can be generated from a polymer and a cross-linking agent for cross linking of the polymer. For instance, a diallyl terminated compound can serve as a cross linking agent for a polysiloxane having a backbone that includes one or more silicons bonded to a hydrogen. Examples of suitable diallyl terminated cross-linking agents include, but are not limited to, diallyl-terminated siloxanes; diallyl terminated polysiloxanes, diallyl terminated alkylene glycols and diallyl terminated poly(alkylene glycol)s.

[0044] The electrolyte can be generated by preparing a precursor solution that includes the polymer, the cross linking agent, the one or more siloxanes and one or more salts. The precursor solution can also optionally be generated so as to include one or more catalysts and/or one or more additives. Suitable catalysts include, but are not limited to, platinum catalysts such as Karlstedt's catalyst and  $\text{H}_2\text{PtCl}_6$ . In some instances, an inhibitor is added to the precursor solution to slow the cross-linking reaction enough to permit handling prior to viscosity changing. Suitable inhibitors include, but are not limited to, dibutyl maleate. In some instances, heat and/or UV energy is also applied to the precursor solution during the reaction of the cross linking precursor and the cross-linking agent.

[0045] A network polymer suitable for the interpenetrating network can be formed using other precursors. For instance, the network polymer can be generated from a mixture of monomers and cross-linking agents that are different from one another. The monomers can polymerize and the cross-linking agents can provide cross linking of the resulting polymer. In another example, monomers that heteropolymerize are employed to generate the network polymer. Other examples of methods for generating electrolytes and electrochemical devices that include network polymers are described in U.S. Patent application serial number 10/104,352, filed on March 22, 2002, entitled "Solid Polymer Electrolyte and Method of Preparation" and incorporated herein by reference in its entirety.

[0046] As noted above, the electrolyte can include one or more solid polymers in addition to the siloxane. A suitable solid polymer is an aprotic polar polymer or aprotic rubbery polymer that by itself is a solid at room temperature. As a result, the ratio of solid polymer to the other electrolyte components can be selected so as to provide an electrolyte that is a solid at room temperature. Examples of suitable solid polymers include, but are not limited to, polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene), polystyrene, polyvinyl chloride, poly(alkyl



methacrylate), poly(alkyl acrylate), styrene butadiene rubber (SBR), poly(vinyl acetate), poly(ethylene oxide) (PEO) and mixtures thereof.

[0047] An electrolyte that includes one or more solid polymers can be generated from a precursor solution. In one example, the precursor solution is formed by mixing one or more siloxanes and a solution that includes a solid polymer. The solution that includes the solid polymer can be generated by dissolving the solid polymer in a solvent such as N-methylpyrrolidone (NMP), dimethyl formamide, dimethyl acetamide, tetrahydrofuran, acetonitrile, and/or water. An additive can also be optionally added to the precursor solution. One or more salts can be added to the precursor solution or the salt can be dissolved in a component of the precursor solution before adding the component to the precursor solution. A solid electrolyte can be formed by evaporating the solvent from the precursor solution.

[0048] An electrolyte that includes one or more solid polymers can also be generated by polymerizing a solid polymer in the presence of the siloxane. For instance, a precursor solution can be generated by mixing the siloxane monomers for the solid polymer and a radical initiator. Suitable radical initiators include, but are not limited to, thermal initiators including azo compounds such as azoisobutyronitrile, peroxide compounds such as benzoylperoxide, and bismaleimide. An additive can also be optionally added to the precursor solution. One or more salts can be added to the precursor solution or the salt can be dissolved in a component of the precursor solution before adding the component to the precursor solution. The electrolyte can be formed by polymerizing the monomers. As an example, an acrylonitrile monomers can be mixed with the siloxane. The acrylonitrile monomers can be polymerized by the application of heat and/or UV to form an electrolyte having a polyacrylonitrile solid polymer.

[0049] As is evident from the above discussion, the electrolyte can include components in addition to the one or more siloxanes. In some instances, the electrolyte is generated such that the one or more siloxanes are more than 20 wt% of the electrolyte, more than 50 wt% of the electrolyte, more than 80 wt% of the electrolyte or more than 95 wt% of the electrolyte.

#### [0050] EXAMPLE 1

[0051] A siloxane was generated using a platinum complex catalyzed hydrosilylation reaction. The siloxane had a structure according to Formula I where: each Z, R and R<sub>4</sub> is a methyl group; R<sub>2</sub> has a structure according to:  $-(CH_2)_3-$ ; R<sub>3</sub> is a hydrogen; and x is 7.

Bis(trimethylsiloxy)methylsilane (11.12 g, Gelest, Inc.) and allyl terminated hepta(ethyleneglycol) methyl ether (23.4 g) were mixed under nitrogen in a flame-dried flask. The mixture was stirred vigorously, and platinum divinyltetramethyldisiloxane (Pt(dvs)) (Aldrich Chem. Co., 3% solution in xylene) was injected into the mixture using a syringe and the temperature was gradually raised to 70-75°C. The reaction mixture was continuously stirred at this temperature for about 24 hours until consumption of the Si-H groups on the starting silane was confirmed by  $^1\text{H}$ -NMR at round 4.7 ppm. After removal of the excess allyl terminated hepta(ethyleneglycol) methyl ether and its isomers by Kugelrohr distillation at 120°C under reduced pressure of about 0.1 mm Hg. The structure of the resulting siloxane was confirmed by the  $^{29}\text{Si}$ -NMR shown in Figure 2A. The siloxane compound had a viscosity of 16.1 cP at 24°C.

[0052] EXAMPLE 2

[0053] A siloxane was generated with a structure according to Formula III where:  $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$ ,  $\text{R}_{16}$  and  $\text{R}_{19}$  are methyl groups;  $\text{R}_{12}$  and  $\text{R}_{17}$  each has as a structure according to:  $-(\text{CH}_2)_3-$ ;  $\text{R}_{13}$  and  $\text{R}_{18}$  are each a hydrogen,  $x$  is 2 and  $y$  is 2. The siloxane was generated according to the method of Figure 1 with  $\text{R}_{20}$  being  $-\text{CH}_2-$ . Tetramethyldisiloxane (13.4 g, 0.2 mole Si-H, Gelest Inc.) and 38.4 g of di(ethylene glycol) allyl methyl ether (0.24 mole, 20% excess) were added to an oven-dried, three-necked 100-mL flask. Dicyclopentadieneplatinum (II) dichloride (500 ppm of  $7.5 \times 10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solution) was injected and the reaction mixture was heated to and stirred at 75°C. Aliquots were taken periodically and the hydrosilylation reaction was monitored by  $^1\text{H}$ -NMR measurements. The absence of Si-H absorption at 4.7 ppm on the  $^1\text{H}$  NMR spectra signaled the completion of the reaction. Excess di(ethylene glycol) allyl methyl ether and its isomers were removed by Kugelrohr distillation to afford a crude product as a brownish yellow liquid, which was then decolorized by activated charcoal in refluxing toluene. The structure of the resulting siloxane was confirmed by FTIR and the  $^1\text{H}$ -NMR spectra shown in Figure 2B. The product siloxane was a colorless liquid with a viscosity of 2.4 cP at 24°C.

[0054] EXAMPLE 3

[0055] A siloxane was generated with a structure according to Formula III where:  $\text{R}_{10}$ ,  $\text{R}_{11}$ ,  $\text{R}_{14}$ ,  $\text{R}_{15}$ ,  $\text{R}_{16}$  and  $\text{R}_{19}$  are methyl groups;  $\text{R}_{12}$  and  $\text{R}_{17}$  each has as a structure according to:  $-(\text{CH}_2)_3-$ ;  $\text{R}_{13}$  and  $\text{R}_{18}$  are each hydrogen,  $x$  is 3 and  $y$  is 3. The siloxane was generated according

to the method of Figure 1 with  $R_{20}$  being  $-\text{CH}_2-$ . Tetramethyldisiloxane (13.4 g, 0.2 mole Si-H, Gelest) and 48.96 g tri(ethylene glycol) allyl methyl ether (48.96 g, 0.24 mole, 20% excess) were added to an oven-dried, three-necked 100 mL flask by syringe. Dicyclopentadieneplatinum (II) dichloride (500 ppm of  $7.5 \times 10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solution) was injected and the reaction solution was heated to and stirred at  $75^\circ\text{C}$ . Aliquots were taken periodically and the hydrosilylation reaction was monitored by  $^1\text{H}$ -NMR measurements. The absence of Si-H absorption at 4.7 ppm on the  $^1\text{H}$  NMR spectra signaled the completion of the reaction. The excess tri(ethylene glycol) allyl methyl ether and its isomers were removed by Kugelrohr distillation to afford a crude product of a brownish yellow liquid which was decolorized by activated charcoal in refluxing toluene. The structure of the resulting siloxane was confirmed by FTIR and the  $^1\text{H}$ -NMR spectra shown in Figure 2B. The product siloxane was a colorless liquid with a viscosity of 6.0 cP at  $24^\circ\text{C}$ .

#### [0056] EXAMPLE 4

[0057] A siloxane was generated with a structure according to Formula III where:  $R_{10}$ ,  $R_{11}$ ,  $R_{14}$ ,  $R_{15}$ ,  $R_{16}$  and  $R_{19}$  are methyl groups;  $R_{12}$  and  $R_{17}$  each has as a structure according to:  $-(\text{CH}_2)_3-$ ;  $R_{13}$  and  $R_{18}$  are each hydrogen,  $x$  is 5, and  $y$  is 5. The siloxane was generated according to the method of Figure 1 with  $R_{20}$  being  $-\text{CH}_2-$ . Tetramethyldisiloxane (3.35 g, 0.05 mole Si-H, Gelest) and 17.52 g of penta(ethylene glycol) allyl methyl ether (0.06 mole, 20% excess) were added to an oven-dried, three-necked 50 mL flask. Dicyclopentadieneplatinum (II) dichloride (100 ppm of  $7.5 \times 10^{-3}$  M  $\text{CH}_2\text{Cl}_2$  solution) was injected and the reaction solution was heated to and stirred at  $80^\circ\text{C}$ . Aliquots were taken periodically and the hydrosilylation reaction was monitored by  $^1\text{H}$ -NMR measurements. The absence of Si-H absorption at 4.7 ppm on the  $^1\text{H}$  NMR spectra signaled the completion of the reaction. The excess penta(ethylene glycol) allyl methyl ether and its isomers were removed by Kugelrohr distillation to afford the crude product as a brownish yellow liquid, which was then decolorized by activated charcoal in refluxing toluene. The structure of the resulting siloxane was confirmed by FTIR and  $^1\text{H}$ -NMR spectra. The product siloxane was a light yellow liquid.

**[0058] EXAMPLE 5**

**[0059]** A siloxane was generated with a structure according to Formula III where:  $R_{10}$ ,  $R_{11}$ ,  $R_{14}$ ,  $R_{15}$ ,  $R_{16}$  and  $R_{19}$  are methyl groups;  $R_{12}$  and  $R_{17}$  each has as a structure according to:  $-(CH_2)_3-$ ;  $R_{13}$  and  $R_{18}$  are each hydrogen,  $x$  is 7 and  $y$  is 7. The siloxane was generated according to the method of Figure 1 with  $R_{20}$  being  $-CH_2-$ . Tetramethyldisiloxane (6.7 g, 0.1 mole Si-H, Gelest) and 46.8 g of poly(ethylene glycol) allyl methyl ether (0.12 mole, 20% in excess, Mw 390) were added to an oven-dried, three-necked 100 mL flask by syringe. Dicyclopentadieneplatinum (II) dichloride (200 ppm of  $7.5 \times 10^{-3}$  M  $CH_2Cl_2$  solution) was injected and the reaction solution was heated to and stirred at  $80^\circ C$ . Aliquots were taken periodically and the hydrosilylation reaction was monitored by  $^1H$ -NMR measurements. The absence of Si-H absorption at 4.7 ppm on the  $^1H$  NMR spectra signaled the completion of the reaction. Then, the excess hepta(ethylene glycol) allyl methyl ether and its isomers were removed by Kugelrohr distillation to afford the crude product as brown liquid, which was then decolorized by activated charcoal in refluxing toluene for 24 hours. The structure of the resulting siloxane was confirmed by FTIR and the  $^1H$ -NMR spectra shown in Figure 2B. The product siloxane was a light yellow liquid with a viscosity of 32.4 cP at  $24^\circ C$ .

**[0060] EXAMPLE 6**

**[0061]**  $LiN(SO_2CF_3)_2$  (LiTFSI) salt was dissolved at room temperature in the siloxane of Example 2, Example 3, and Example 4 to make electrolytes that each have an  $[EO]/[Li]$  ratio of 15. The ionic conductivity of the electrolytes were measured by use of ac impedance spectrum in the form of 2032 button cell assembled by filling the Teflon O-ring between two stainless steel discs with the electrolytes. Figure 3A shows the ionic conductivity for each of the electrolytes as a function of temperature. The electrolytes show an ionic conductivity of about  $4.1 \times 10^{-4}$  S/cm at  $37^\circ C$ .

**[0062] EXAMPLE 7**

**[0063]** An electrolyte was prepared by dissolving  $LiN(SO_2CF_3)_2$  (LiTFSI) to 1M in the siloxane of Example 1. The ionic conductivity of the electrolyte was measured by use of ac impedance spectrum in the form of 2032 button cell assembled by filling the Teflon O-ring

between two stainless steel discs with the electrolyte. Figure 3B shows the ionic conductivity of the electrolyte as a function of temperature. The siloxane electrolyte shows an ionic conductivity of around  $3 \times 10^{-4}$  S/cm at 37°C.

[0064] EXAMPLE 8

[0065] A variety of electrolytes were generated by dissolving Bis(oxalato)borate (LiBOB) in different siloxanes. Each of the siloxanes has a structure according to Formula II where Z, R<sub>5</sub>, R<sub>6</sub>, R<sub>9</sub> are each a methyl group; R<sub>8</sub> is a hydrogen and R<sub>7</sub> is triethylene group (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-). In one of the electrolytes x is 2, in another electrolyte x is 3 and in another electrolyte x is 7. In each electrolyte, the LiBOB was dissolved so as to have an [ethylene oxide]/[Li] ratio of 15. The ionic conductivity of the electrolytes were measured by use of ac impedance spectrum in the form of 2032 button cell assembled by filling the Teflon O-ring between two stainless steel discs with the electrolyte. Figure 3C shows the ionic conductivity of the electrolyte as a function of temperature. The electrolytes show an ionic conductivity of about  $4.5 \times 10^{-4}$  S/cm at 37 °C.

[0066] EXAMPLE 9

[0067] The electrochemical stability window of the electrolyte of Example 7 was determined by cyclic voltammetry with 2032 button cell made by sandwiching the electrolyte between a stainless steel disc (as a working electrode) and a lithium metal disc (as the counter and reference electrodes). Porous polypropylene membrane (Celgard 3501) was used as a separator. Three cycles of cyclic voltammetry test were conducted. Figure 4 shows the electrochemical stability of the electrolyte. The electrolyte was stable up to 4.5 V without significant decomposition.

[0068] EXAMPLE 10

[0069] A lithium cell was prepared with a Li metal anode and a cathode activated by an electrolyte having lithium bis(oxalato)borate (LiBOB) dissolved to 0.8 M in the siloxane of Example 1. The composition of the cathode was 84wt% LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>, 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black. The effective cell area was 1.6 cm<sup>2</sup>. Figure 5 shows the charge/discharge profile of the cell. The charge and discharge rate was C/20 (0.1 mA). The siloxane compound generates a discharge cathode capacity of close to 150 mAh/g.

**[0070] EXAMPLE 11**

**[0071]** A lithium secondary cell was prepared with an anode and a cathode activated by an electrolyte having lithium bis(oxalato)borate (LiBOB) dissolved to 0.8 M in the siloxane of Example 1. The composition of the cathode was 84wt%  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black. The composition of the anode was 92wt% MCMB and 8wt% PVDF binder. The effective cell area was  $1.6 \text{ cm}^2$ . Figure 6 shows the charge/discharge profile of the cell. The electrolyte shows good compatibility with MCMB graphite carbon having a discharge cathode capacity of above 150 mAh/g.

**[0072] EXAMPLE 12**

**[0073]** A lithium cell was prepared with a Li metal anode and a cathode activated by an electrolyte having lithium bis(oxalato)borate (LiBOB) dissolved to 0.8 M in the siloxane of Example 1. The composition of the cathode was 84wt%  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , 8wt% PVDF binder, 4wt% SFG-6 graphite and 4wt% carbon black. The effective cell area was  $1.6 \text{ cm}^2$ . Figure 7 shows the cycle performance of the cell. The charge and discharge rate was C/20 (0.1 mA) and the test was conducted at  $37^\circ\text{C}$ . The cell shows good cycle ability with a cell capacity of above 150 mAh/g based on the positive material.

**[0074]** The electrolytes described above can be used in electrochemical devices. For instance, the electrolytes can be used as the electrolyte of batteries, capacitors, and hybrid capacitor/batteries. As an example, the electrolyte can be applied to batteries in the same way as carbonate-based electrolytes. Batteries with a liquid electrolyte can be fabricated by injecting the electrolyte into a spiral wound cell or prismatic type cell. The electrolyte can be also coated onto the surface of electrodes and assembled with a porous separator to fabricate a single or multi-stacked cell that can enable the use of flexible packaging.

**[0075]** The solid electrolytes described above can also be applied to electrochemical devices in the same way as solid carbonate-based electrolytes. For instance, a precursor solution having components for a solid electrolyte can be applied to one or more substrates. Suitable substrates include, but are not limited to, anodes, cathodes and/or separators such as a polyolefin separator, nonwoven separator or polycarbonate separator. The precursor solution is converted to a solid or

gel electrolyte such that a film of the electrolyte is present on the one or more substrates. In some instances, the substrate is heated to solidify the electrolyte on the substrate. An electrochemical cell can be formed by positioning a separator between an anode and a cathode such that the electrolyte contacts the anode and the cathode. [REDACTED]

[REDACTED]

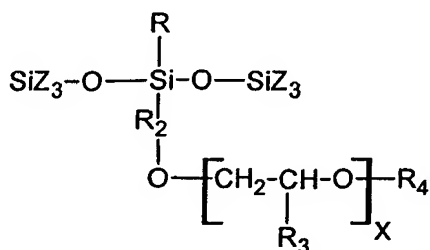
[0076] An example of a suitable secondary lithium battery construction includes one or more lithium metal oxide cathodes, porous separators, and one or more anodes made of carbon, lithium metal, or combinations thereof. Cathodes may include  $\text{Li}_x\text{VO}_y$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_y\text{Me}_z\text{O}_2$ ,  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ,  $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{O}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFeO}_2$ ,  $\text{LiMc}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , vanadium oxide, carbon fluoride and mixtures thereof wherein Me is Al, Mg, Ti, B, Ga, Si, Mn, Zn, and Mc is divalent metal such as Ni and Co, Fe, Cr, or Cu. Anodes may include graphite, soft carbon, hard carbon,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , tin alloys, silica alloys, intermetallic compounds, lithium metal, lithium metal alloys, and combinations thereof.

[0077] Other embodiments, combinations and modifications of this invention will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, this invention is to be limited only by the following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying drawings.

## CLAIMS

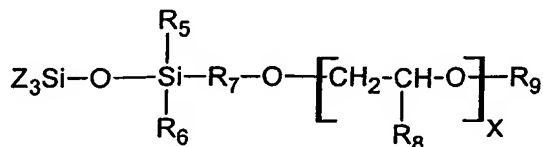
We claim:

1. An electrochemical device, comprising:  
an electrolyte including a siloxane having two or three silicons, at least one of the silicons being linked to one or more side chains that include a poly(alkylene oxide) moiety.
2. The device of claim 1, wherein the siloxane is one of a plurality of siloxanes in the electrolyte.
3. The device of claim 1, wherein the siloxane includes a plurality of side chains that each include a poly(alkylene oxide) moiety.
4. The device of claim 1, wherein the siloxane includes three silicons.
5. The device of claim 1, wherein the siloxane has a structure selected from a group consisting of structures represented by formula I through formula III:



formula I:

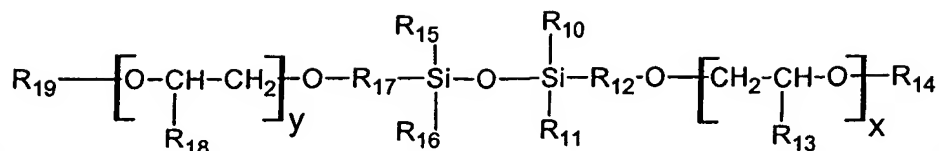
where R is an alkyl group; R<sub>2</sub> is an organic spacer; R<sub>3</sub> is a hydrogen atom or an alkyl group; R<sub>4</sub> is an alkyl group; Z is an alkyl or an aryl group and x is from 1 to 30;



formula II:

where R<sub>5</sub> is an alkyl group; R<sub>6</sub> is an alkyl group; R<sub>7</sub> is a spacer; R<sub>8</sub> is a hydrogen atom or an alkyl group; R<sub>9</sub> is an alkyl group; Z is an alkyl or an aryl group and x is from 1 to 30; and





formula III:

where

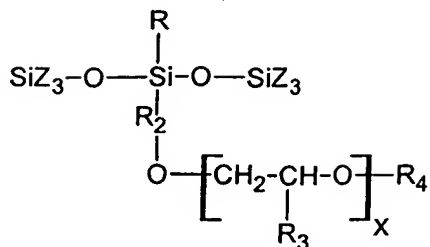
$R_{10}$  is an alkyl group;  $R_{11}$  is an alkyl group;  $R_{12}$  is an organic spacer;  $R_{13}$  is a hydrogen atom or an alkyl group;  $R_{14}$  is an alkyl group;  $R_{15}$  is an alkyl group;  $R_{16}$  is an alkyl group;  $R_{17}$  is an organic spacer;  $R_{18}$  is a hydrogen atom or an alkyl group;  $R_{19}$  is an alkyl group;  $x$  is from 1 to 30 and  $y$  is from 1 to 30.

6. The device of claim 5, wherein the siloxane has a structure selected from the group consisting of structures represented by formula I.
7. The device of claim 5, wherein the siloxane has a structure selected from the group consisting of structures represented by formula II.
8. The device of claim 5, wherein the siloxane has a structure selected from the group consisting of structures represented by formula III.
9. The device of claim 5, wherein  $R_2$ ,  $R_7$ ,  $R_{12}$  and  $R_{17}$  are selected from a group consisting of alkylenes.
10. The device of claim 5, wherein  $R_2$ ,  $R_7$ ,  $R_{12}$  and  $R_{17}$  have a structure according to  $-(CH_2)_3-$ .
11. The device of claim 1, wherein the electrolyte includes an alkali metal salt.
12. The device of claim 11, wherein a concentration of the alkali metal salt in the electrolyte is in a range of 0.3M to 2.0 M.
13. The device of claim 11, wherein the alkali metal salt is a lithium salt.
14. The device of claim 13, wherein the lithium salt is selected from a group consisting of:  $LiClO_4$ ,  $LiBF_4$ ,  $LiAsF_6$ ,  $LiPF_6$ ,  $LiSO_3CF_3$ ,  $LiN(CF_3SO_2)_2$ ,  $LiC(SO_2CF_3)_3$ ,  $LiN(SO_2C_2F_5)_2$ ,

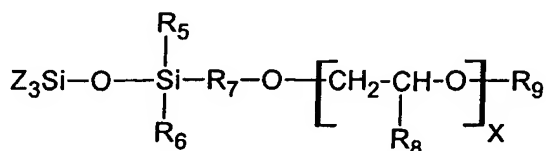
lithium alkyl fluorophosphates, lithium bis(oxalato)borate (LiBOB), other lithium bis(chelato)borates, and mixtures thereof.

15. The device of claim 1, further comprising:  
at least one cathode, at least one porous separator and at least one anode.
16. The device of claim 15, wherein the cathode includes a lithium metal oxide and the anode includes at least one material selected from a group consisting of carbon and lithium metal.
17. The device of claim 15, wherein the cathode includes one or more materials selected from a group consisting of:  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_y\text{Me}_z\text{O}_2$ ,  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ ,  $\text{LiMn}_{0.3}\text{Co}_{0.3}\text{Ni}_{0.3}\text{O}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFeO}_2$ ,  $\text{LiMc}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , vanadium oxide, carbon fluoride and mixtures thereof, wherein Me is Al, Mg, Ti, B, Ga, Si etc. and Mc is a divalent metal.
18. The device of claim 15, wherein the anode includes one or more materials selected from a group consisting of: graphite, carbon,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , tin alloys, silica alloys, intermetallic compounds, lithium metal, and mixtures thereof.
19. The device of claim 1, wherein the electrolyte is a liquid.
20. The device of claim 1, wherein the electrolyte is a solid.
21. The device of claim 20, wherein the electrolyte includes the siloxane entrapped within a network polymer.
22. The device of claim 21, wherein the network polymer is a product of polymerizing a dialkyl acrylate, a dimethacrylate, a dialkyl methacrylate or a diallyl terminated compound.
23. The device of claim 1, wherein the electrolyte includes a solid polymer.

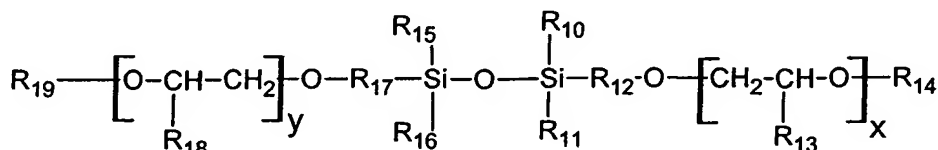
24. The device of claim 23, wherein the solid polymer is selected from a group consisting of: polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinyl acetate), polystyrene, poly(ethylene oxide) (PEO).
25. The device of claim 1, wherein the electrolyte includes an additive configured to form a passivation layer on an electrode.
26. The device of claim 1, wherein the electrolyte includes at least one additive selected from the group consisting of: vinyl carbonate, vinyl ethylene carbonate, ethylene sulfite, 1,3 dimethyl butadiene, styrene carbonate, aromatic carbonates, vinyl pyrrole, vinyl piperazine, vinyl piperidine, vinyl pyridine, and mixtures thereof.
27. The device of claim 1, wherein the electrolyte includes lithium bis(oxalato)borate (LiBOB) and one or more additives selected from the group consisting of vinyl carbonate (VC) and vinyl ethylene carbonate (VEC).
28. The device of claim 1, wherein the siloxane is more than 50 wt% of the electrolyte.
29. The device of claim 1, wherein the electrolyte has an ionic conductivity higher than  $2.0 \times 10^{-4}$  S/cm at 24 °C.
30. A method of forming an electrochemical device, comprising:  
generating an electrolyte including a siloxane having two or three silicons, at least one of the silicons being linked to one or more side chains that include a poly(alkylene oxide) moiety;  
and  
activating at least one anode and at least one cathode with the electrolyte.
31. The method of claim 30, wherein the siloxane has a structure selected from a group consisting of structures represented by formula I through formula III:



formula I: where R is an alkyl group; R<sub>2</sub> is an organic spacer; R<sub>3</sub> is a hydrogen atom or an alkyl group; R<sub>4</sub> is an alkyl group; Z is an alkyl or an aryl group and x is from 1 to 30;



formula II: where R<sub>5</sub> is an alkyl group; R<sub>6</sub> is an alkyl group; R<sub>7</sub> is a spacer; R<sub>8</sub> is a hydrogen atom or an alkyl group; R<sub>9</sub> is an alkyl group; Z is an alkyl or an aryl group and x is from 1 to 30; and



formula III: where R<sub>10</sub> is an alkyl group; R<sub>11</sub> is an alkyl group; R<sub>12</sub> is an organic spacer; R<sub>13</sub> is a hydrogen atom or an alkyl group; R<sub>14</sub> is an alkyl group; R<sub>15</sub> is an alkyl group; R<sub>16</sub> is an alkyl group; R<sub>17</sub> is an organic spacer; R<sub>18</sub> is a hydrogen atom or an alkyl group; R<sub>19</sub> is an alkyl group; x is from 1 to 30 and y is from 1 to 30.

32. The method of claim 31, wherein the siloxane has a structure selected from the group consisting of structures represented by formula I.

33. The method of claim 31, wherein the siloxane has a structure selected from the group consisting of structures represented by formula II.

34. The method of claim 31, wherein the siloxane has a structure selected from the group consisting of structures represented by formula III.

35. The method of claim 31, wherein  $R_2$ ,  $R_7$ ,  $R_{12}$  and  $R_{17}$  are selected from a group consisting of alkylenes.
36. The method of claim 31, wherein  $R_2$ ,  $R_7$ ,  $R_{12}$  and  $R_{17}$  have a structure according to  $-(CH_2)_3-$ .
37. The method of claim 30, wherein generating the electrolyte includes dissolving an alkali metal salt in the siloxane.
38. The method of claim 37, wherein the salt is selected from a group consisting of:  $LiClO_4$ ,  $LiBF_4$ ,  $LiAsF_6$ ,  $LiPF_6$ ,  $LiSO_3CF_3$ ,  $LiN(CF_3SO_2)_2$ ,  $LiC(SO_2CF_3)_3$ ,  $LiN(SO_2C_2F_5)_2$ , lithium alkyl fluorophosphates, lithium bis(oxalato)borate (LiBOB), other lithium bis(chelato)borates, and mixtures thereof.
39. The method of claim 30, wherein at least one cathode includes a lithium metal oxide and at least one anode includes at least one material selected from a group consisting of carbon and lithium metal.
40. The method of claim 30, wherein at least one cathode includes one or more materials selected from a group consisting of:  $LiCoO_2$ ,  $LiNiO_2$ ,  $LiNi_{1-x}Co_yMe_zO_2$ ,  $LiMn_{0.5}Ni_{0.5}O_2$ ,  $LiMn_{0.3}Co_{0.3}Ni_{0.3}O_2$ ,  $LiFePO_4$ ,  $LiMn_2O_4$ ,  $LiFeO_2$ ,  $LiMc_{0.5}Mn_{1.5}O_4$ , vanadium oxide, carbon fluoride and mixtures thereof, wherein Me is Al, Mg, Ti, B, Ga, Si etc. and Mc is a divalent metal.
41. The method of claim 30, wherein at least one anode includes one or more materials selected from a group consisting of: graphite, carbon,  $Li_4Ti_5O_{12}$ , tin alloys, silica alloys, intermetallic compounds, lithium metal, and mixtures thereof.
42. The method of claim 30, wherein the electrolyte is a liquid.
43. The method of claim 30, wherein the electrolyte is a solid.

44. The method of claim 43, wherein the electrolyte includes the siloxane entrapped within a network polymer.

45. The method of claim 44, wherein the network polymer is a product of polymerizing a dialkyl acrylate, a dimethacrylate, a dialkyl methacrylate or a diallyl terminated compound.

46. The method of claim 30, wherein the electrolyte includes a solid polymer selected from a group consisting of: polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinyl acetate), polystyrene, poly(ethylene oxide) (PEO).

47. The method of claim 30, wherein the electrolyte includes at least one additive selected from the group consisting of: vinyl carbonate, vinyl ethylene carbonate, ethylene sulfite, 1,3 dimethyl butadiene, styrene carbonate, aromatic carbonates, vinyl pyrrole, vinyl piperazine, vinyl piperidine, vinyl pyridine, and mixtures thereof.

## SILOXANE BASED ELECTROLYTES FOR USE IN ELECTROCHEMICAL DEVICES

## ABSTRACT

The electrolyte includes a siloxane activating an anode and a cathode. The siloxane has two or three silicons. At least one of the silicons is linked to one or more side chains that include a poly(alkylene oxide) moiety. The electrolyte can be a solid or a liquid. In some instances, the electrolyte is employed in a secondary battery.

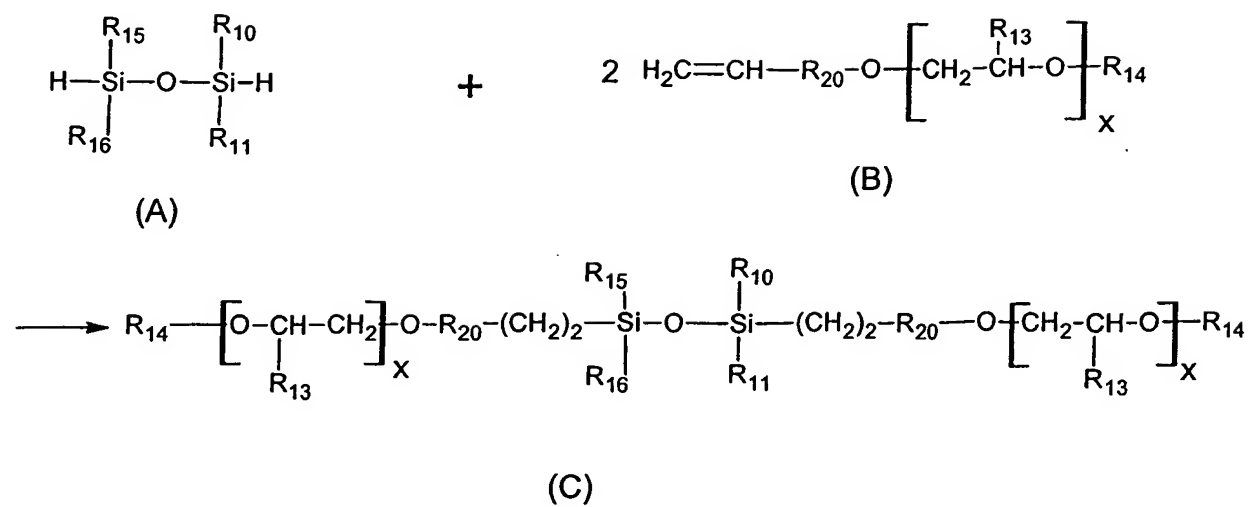
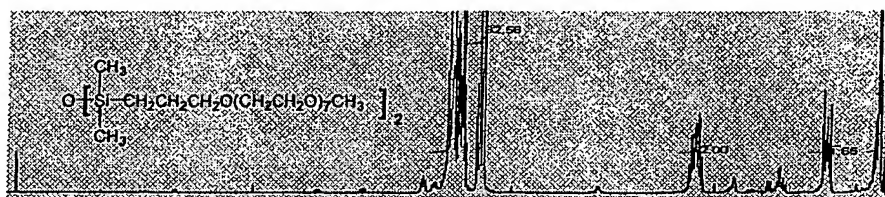
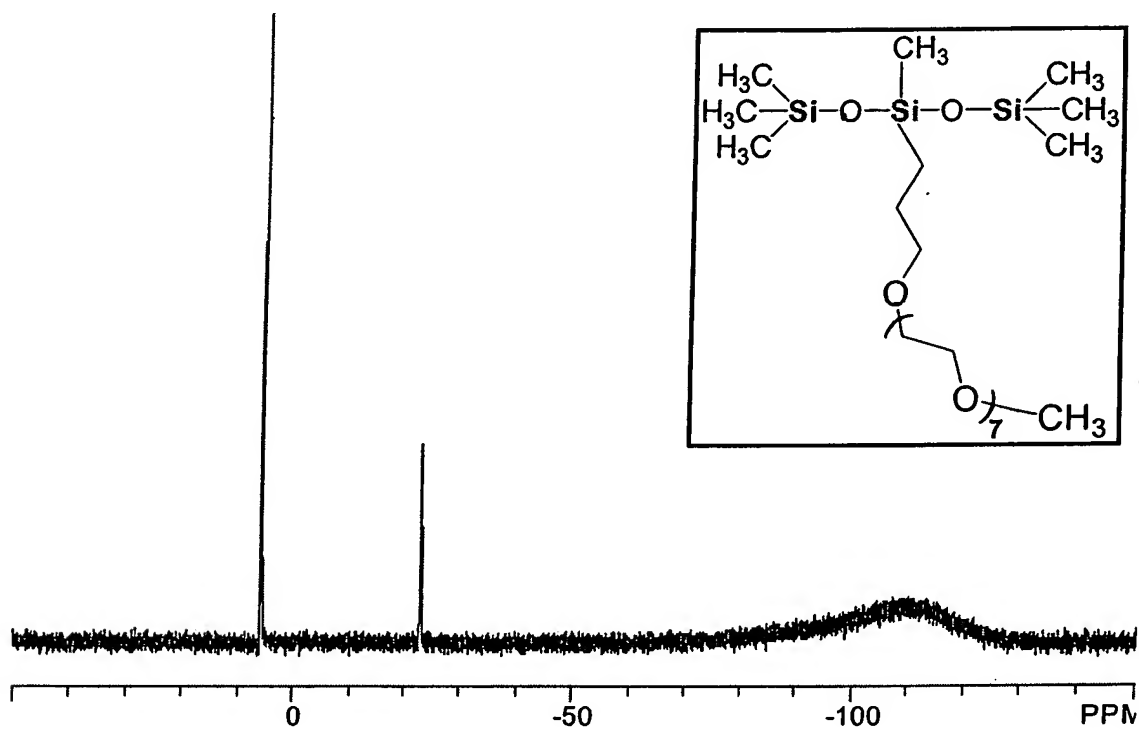


Figure 1







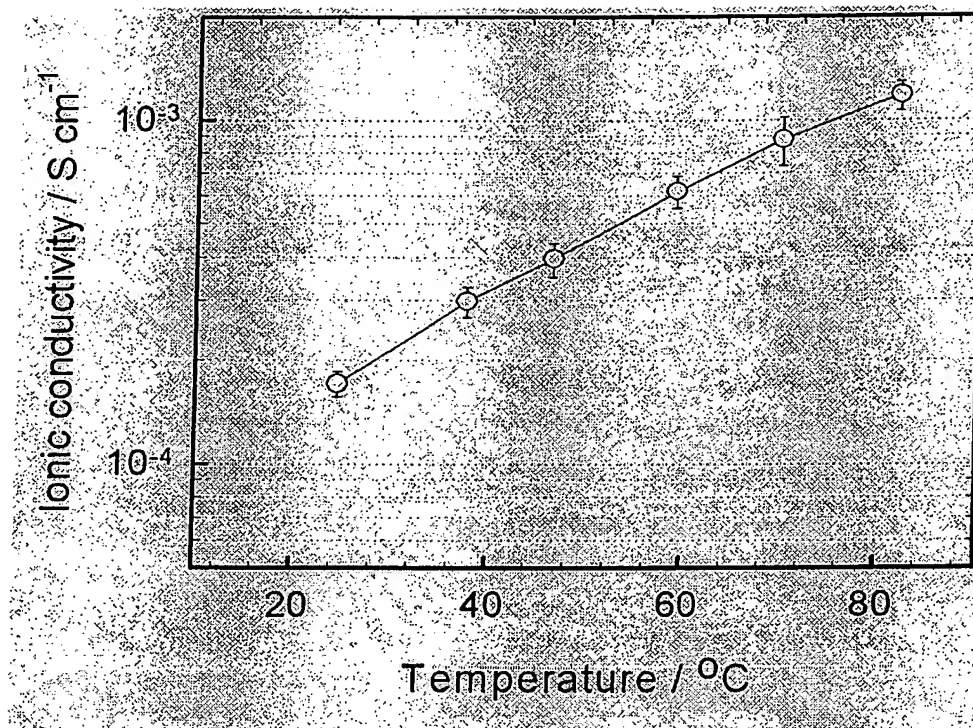


Figure 3B

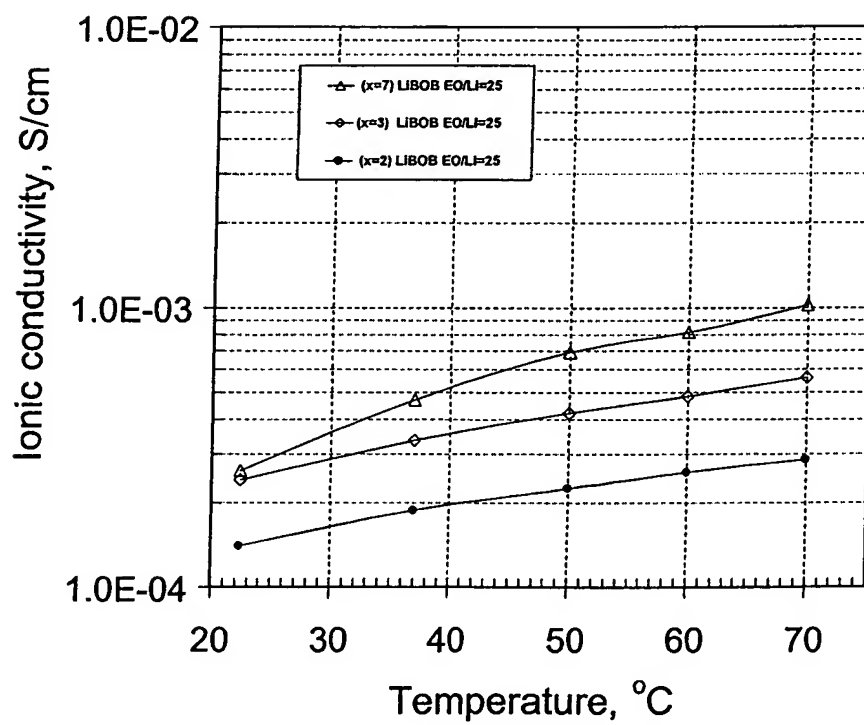


Figure 3C

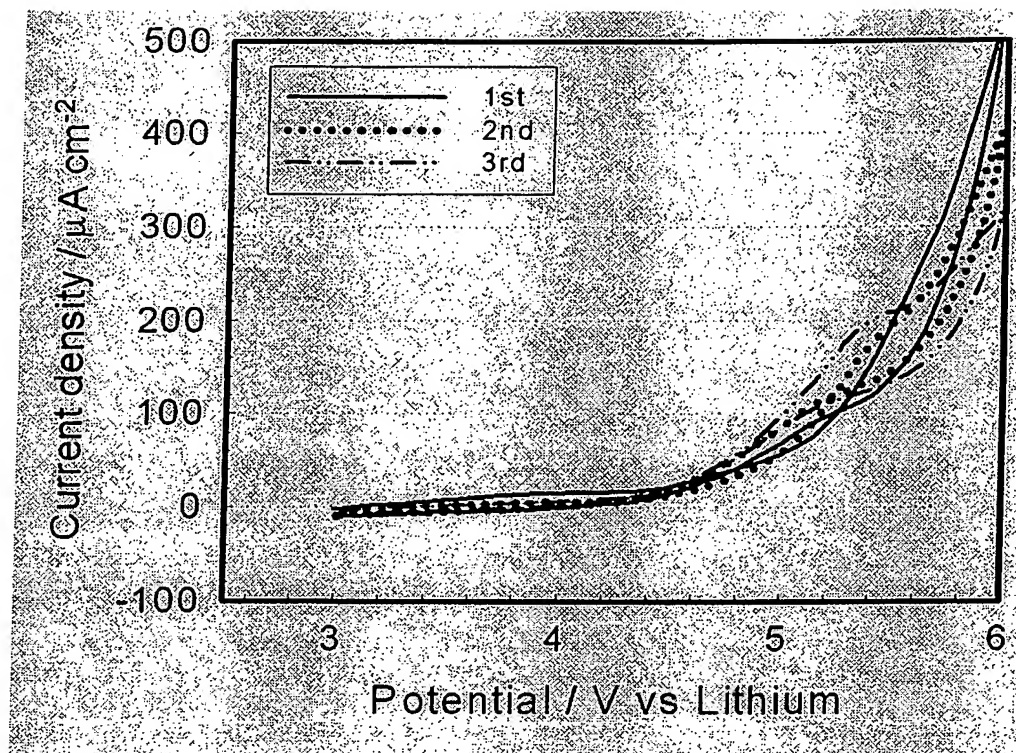


Figure 4

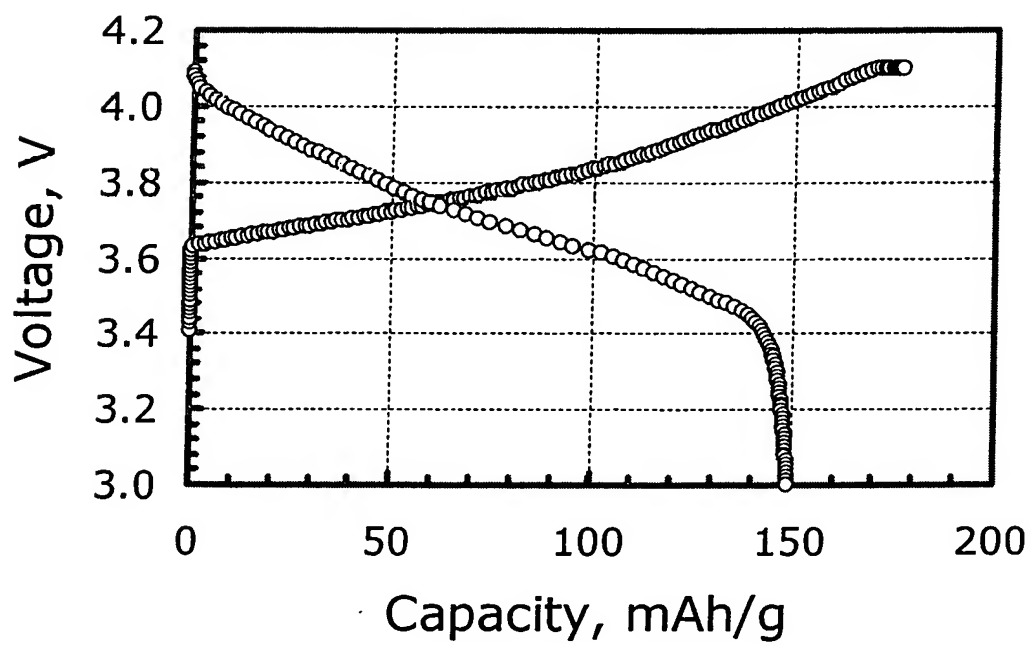


Figure 5

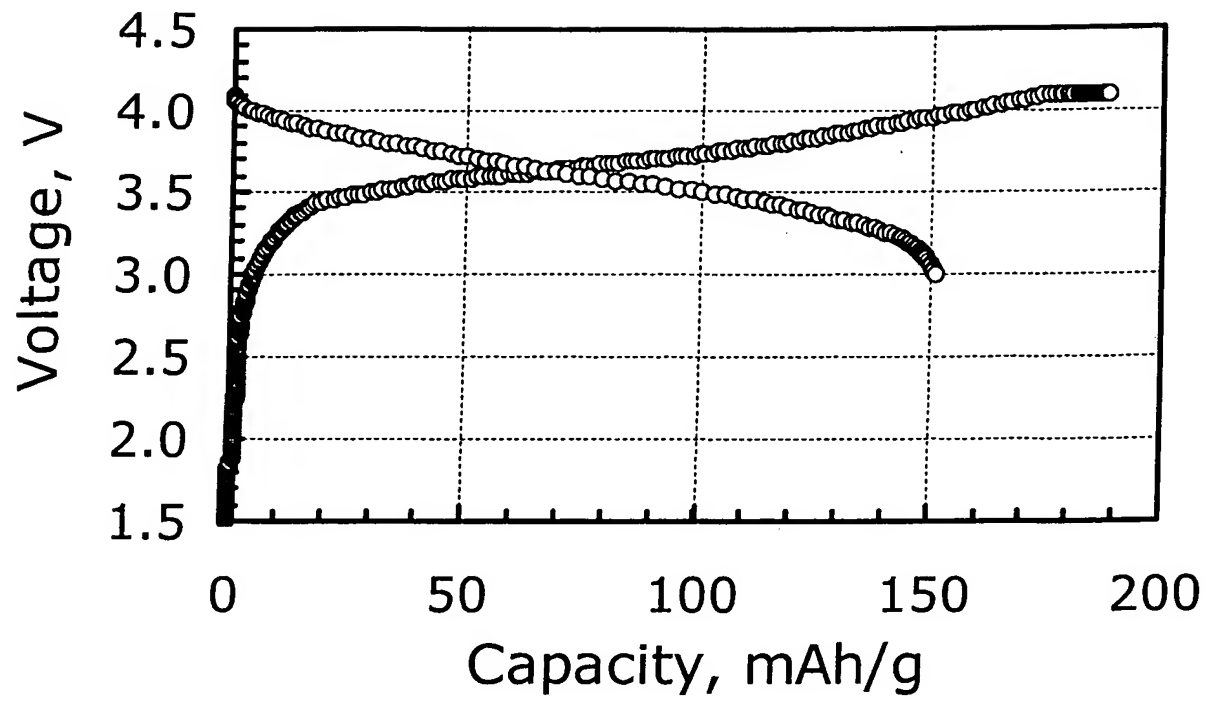


Figure 6

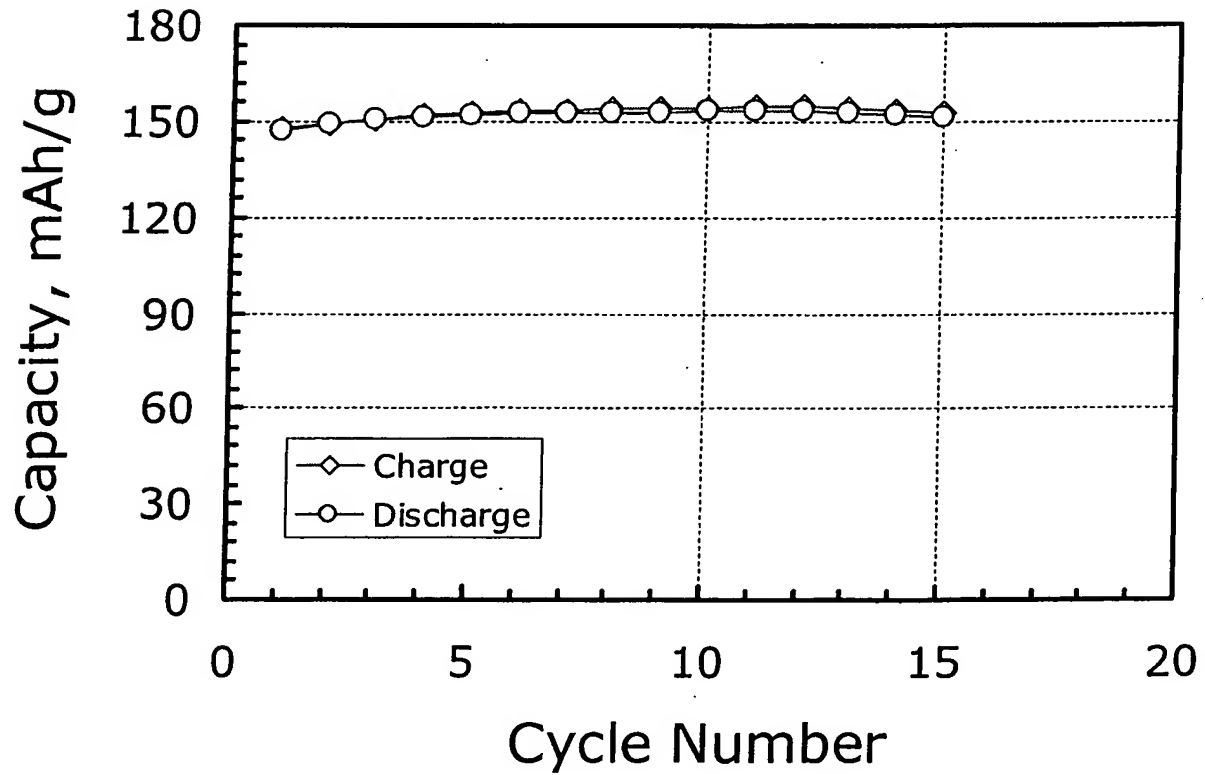


Figure 7



# DECLARATION

## 2